^{31}P N.M.R. Study of Tertiary Phosphine Complexes of Gold(I)

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Summary The stoicheiometry and exchange behaviour of the gold(I)–tertiary phosphine systems [AuBr(L)] and [Au(L)$_n$]Br depend critically on the steric and electronic properties of the ligand.

GOLD(I) is commonly two-co-ordinate, but evidence for higher co-ordination numbers is growing, particularly from ^{31}P n.m.r.[1,2] and ^{197}Au Mössbauer[3–5] spectroscopy. With PPh$_3$,[5] P(C$_6$H$_4$Me-p)$_3$,[1] or PEt$_3$[2] as ligand, two-, three-, and four-co-ordinate species have been detected. However, the ^{31}P n.m.r. study we now present shows that the maximum co-ordination number attainable depends on the particular ligand used. Ligand-exchange relaxation also shows marked ligand dependence. We have employed P(C$_6$H$_{11}$)$_3$ (C$_6$H$_{11}$ = cyclohexyl), PBu$^n_3$, PMe$_2$Ph, and PMePh$_2$, which were added in various amounts to CHCl$_3$- or CH$_2$Cl$_2$-solutions of [Et$_4$N][AuBr$_2$]. The results are summarized in the Table.

TABLE. ^{31}P Chemical shifts for gold(I) complexes (p.p.m. from 85% H$_3$PO$_4$, −80 °C, CH$_2$Cl$_2$ solutions).

			P:Au		
PR$_3$	1:1	2:1	3:1	4:1	>4:1
P(C$_6$H$_{11}$)$_3$	−56·5	−63·8	a	a	a
PBu$^n_3$	−24·5	−32·7	−29·5	b	b
PMe$_2$Ph	−6·1	−15·6	+22·7	+35·1	b
PMePh$_2$	−18·0	−26·0	−13·8	+5·8	c

[a] Free P(C$_6$H$_{11}$)$_3$ detected, $T < -50$ °C. [b] Rapid exchange at −120 °C. [c] Exchange, $T > -80$ °C.

At a P:Au mole ratio of 1·0:1 or less, the spectra were identical with those of [AuBr(L)] prepared independently. With P(C$_6$H$_{11}$)$_3$ or PBu$^n_3$ at room temperature, addition of further small amounts of ligand led to the growth of a second signal, at the expense of, and downfield from the first. Conversion was complete at P:Au = 2·0:1. A CH$_2$Cl$_2$-solution of [AuBr{P(C$_6$H$_{11}$)$_3$}] containing 1 mol equiv. of P(C$_6$H$_{11}$)$_3$ had an electrical conductivity corresponding to a 1:1 electrolyte. The new species is thus [Au(L)$_2$]Br, and the corresponding chloride and perchlorate had essentially the same chemical shifts. On addition of further small amounts of ligand, the single resonance moved upfield towards that of the free phosphine. When the solution was cooled to −60 °C, for P(C$_6$H$_{11}$)$_3$ two resonances were observed corresponding to [Au(L)$_2$]$^+$ and the free phosphine. With PBu$^n_3$, however, the spectrum resolved below −80 °C into the [Au(L)$_2$]$^+$ signal and another at slightly higher field, not the free ligand, presumably [Au(L)$_3$]$^+$. At P:Au>3·0:1, a single signal was seen, moving to higher field with increasing concentration of the ligand. No signal due to the free phosphine was seen even at −120 °C, showing that [Au(PBu$^n_3$)$_3$]$^+$ undergoes extremely rapid exchange with the phosphine.

For L = PMe$_2$Ph or PMePh$_2$, rapid exchange occurred at room temperature for 1·0:1 <P:Au<4·0:1, but on cooling four different species were detected, according to the stoicheiometry; these are reasonably assigned as [AuBr(L)] and [Au(L)$_n$]Br (n = 2, 3, or 4). The signal for [Au(L)$_4$]$^+$ was at highest field but distinct from that of the free

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ligand. For $PMePh_2$ at P : Au > 4·0 : 1, both $[Au(PMePh_2)_4]^+$ and $PMePh_2$ were seen at low temperature (< −90 °C), but for PMe_2Ph rapid exchange occurred even at −120 °C.

The maximum co-ordination number and the exchange behaviour are thus functions of the ligand. With the bulky $P(C_6H_{11})_3$, only two ligands can be co-ordinated, but $[Au(L)_2]^+$ exchanges rapidly with the free ligand, presumably *via* a transient $[Au(L)_3]^+$ cation. With the less sterically demanding PBu^n_3, a third ligand can be bound but the tris-ligand complex undergoes rapid dissociative exchange at room temperature and, in the presence of an excess of the ligand, exchanges associatively very rapidly. With these two ligands, no exchange occurs between $[AuBr(L)]$ and $[Au(L)_2]^+$ at room temperature. With the softer PMe_2Ph and $PMePh_2$, four complexes are seen but all undergo rapid exchange at room temperature. The complexes $[Au(L)_4]^+$ exchange with free ligand, with PMe_2Ph exchanging faster than $PMePh_2$. The behaviour of the Au^+–PR_3 system thus depends critically on both the steric and electronic properties of the phosphine.

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